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SUMMARY SCREENING REPORT ON CHEMICAL DESTRUCT SYSTEM

AUTHORS: J.A. Roll, R.M. Vollmer & P.H. Wilks

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SUMMARY SCREENING REPORT ON CHEMICAL DESTRUCT SYSTEMS

Introduction:

Following operation of the NERVA core, it is desirable to minimize the deposition of fission products in the earth biosphere. One means of accomplishing this objective is to degrade the core into small particles which will have long residence times above the biosphere and/or high rates of fission product loss during re-entry. Were this accomplished by the introduction of a reactive chemical into the core, uniformly small particles of zero velocity vector would be produced. These are two highly desirable criteria, not readily satisfied by the other types of destruct systems under consideration. Moreover, a chemical destruct system would be relatively immune to radiation damage.

Consequently, a screening program has been carried out at WANL to examine the feasibility of a chemical destruct system for the post-operational disposition of the NERVA core. The first step in this program was a series of free energy calculations to establish which reagents merited laboratory investigation. These calculations were followed by qualitative and semi-quantitative laboratory tests to determine the effect upon fuel samples of all reagents which appeared to be promising from a theoretical standpoint. Two types of fuel were investigated, the first, defined as Type I, consists of 8-10 micron UC_2 particles dispersed in a graphite matrix. Here, advantage could be taken of the preference of many reagents for reaction with UC_2 over that with carbon. Also, reagents which were ineffective against Type I fuel could be eliminated for use against Type II fuel, a more resistant dispersion in graphite of 100 micron UC_2 particles coated with pyrocarbon.

A summary of the results of tests with each reagent is presented. Comments are included on the feasibility of employing each reagent in a chemical destruct system. Where applicable, a discussion of actual full scale system requirements is given.

Summary:

An extensive laboratory screening program has examined theoretically promising reagents from the standpoint of their reactions with fueled materials at temperatures from 20-2450°C. Extrapolation of the data which were obtained results in rejection of most reagents because of the high weight requirements for complete reaction with the core.

The interhalogens hold some promise of core degradation with modest weights of reagent because of their combined action as fluorinating agents and their ability to form interstitial compounds with graphite. Of the interhalogens tested, chlorine trifluoride has proven to be the most promising, having accomplished complete specimen degradation at 240°C with an amount of ClF_3 equal to only 25% of the specimen weight. The capabilities and requirements of a destruct system employing ClF_3 are discussed.

Results:

The theoretical evaluation of reagents, based on free energy calculations (ref. 1), proved to be a desirable approach to this problem. All reagents for which spontaneous reaction was predicted did, in fact, react with the fuel. However, in most cases, the efficiency of the reaction and nature of the products were such that large quantities of reagent were required to effect complete degradation of the fueled specimens. Data from

most of the theoretically promising reagents, employed with Type I fuel without NbC lining, have been reported previously (Ref. 1, 2). A brief summary of the effect of each reagent follows:

Oxygen:

Specimens weighing about one gram were heated in various tests in the range 415-2450°C and allowed to react with oxygen. Both static and flowing oxygen were employed. The oxygen was found not to attack UC_2 preferentially. In a typical test, an amount of oxygen equivalent to 35% of the sample weight left 85% of the sample as a hard core. Extrapolation of the results of this series of tests indicates that a minimum of 6000 pounds of oxygen would be required for a full scale system. Moreover, as the graphite temperature falls below 1500°C, a greater weight of oxygen is required to react with a unit weight of graphite.

Water:

Specimens weighing approximately 20 grams were heated inductively in the range 825-2170°C while immersed in water or bathed in steam. The samples experienced some weight loss but remained generally intact, although large excesses of reagent were present. Consequently, a prohibitive weight of water is indicated for degradation of the entire core.

Hydrogen Peroxide:

A 30% H_2O_2 solution was employed in excess with 0.8 gram specimens of fuel between 20 and 2100°C. The samples remained intact in every case, with some weight loss at higher temperatures. A prohibitive weight of H_2O_2 would be required for reaction with the entire core.

Nitric Acid - Hydrogen Peroxide:

An excess of this strongly oxidizing mixture, employed with a one gram specimen at 20-230°C, failed to damage the specimen's integrity. Since, at higher temperature, the use of this mixture is less favored stoichiometrically than oxygen alone, its weight requirements would be prohibitive.

Hydrogen Chloride:

An excess of HCl vapor reacted with a one gram specimen at 2160°C and accomplished only surface powdering of the specimen. A prohibitive weight of HCl would be required.

Hydrofluoric Acid:

A specimen weighing 0.8 grams was submerged in boiling 10% HF for one hour. The specimen cracked but its strength was not significantly reduced. The use of HF as a chemical destruct agent is precluded.

The above listing essentially summarizes the work up to publication of WANL-TNR-075 (Ref. 1). Most of the tests described below have been performed since that time.

Nitrogen:

Large excesses of dry nitrogen were flowed past 4-5 gram specimens of Type I fuel at 1000-1200°C with less than 10% weight loss in all cases. The weight of nitrogen required to degrade the entire core would be prohibitive.

Boron Tribromide:

Three tests, employing 4 gram specimens of Type I fuel with BBr_3 at 1000-2000°C effected significant weight losses. Extrapolation of these data indicates that 4000 pounds of BBr_3 would be required to degrade on entire core.

Bromine:

Subsequent to tests with excess bromine which yielded encouraging results, a series of quantitative tests was performed. Specimens of Type I fuel weighing 4-5 grams were held at temperatures from 25 to 2000°C while subjected to bromine attack. Results indicated that amounts of bromine in excess of 6000 pounds would be required for effective degradation of the core.

Chlorine:

Excess chlorine was able to powder specimens of Type I fuel at about 500°C. The specimens remained intact at all temperatures up to 2000°C when chlorine weight employed was limited to 50% of the specimen weight. Preferential removal of uranium and daughter nuclides was observed with Type I fuel in the range 15-2000°C. However, no such effect could be obtained with Type II fuel and extrapolated weights necessary even to degrade a core of Type I fuel were prohibitive.

Fluorinated Hydrocarbons:

A series of tests on 3-4 grams specimens of Type I fuel was run with CF_4, CCl_3F, and CCl_2F_2 in the range of 1000-2000°C. Amounts of fluorocarbon ranging from 20-40% of the specimen weight failed to produce a weight loss of as much as 10% or to weaken the specimens at all. On this basis, the weight of fluorocarbon needed for a full scale system would be prohibitive.

Boron Trichloride:

In the range 900-1600°C, using 5 gram samples of Type I fuel, with 1-3 grams of BCl_3, some preferential leaching of daughter nuclides was observed, although the specimens

remained structurally sound. Accordingly, the use of BCl_3 is not advisable.

Chromyl Chloride:

Since compounds such as chromyl chloride are known to form interstitial compounds with graphite, (Ref. 3), from 0.6 to 1.0 gram of CrO_2Cl_2 were employed as a gas with 3-4 gram specimens of Type I fuel at 1000-2000°C. Almost no effect on the fuel was observed. This is probably typical of the graphite-metal halide systems, as their compounds decompose at relatively low temperatures. Since no helpful reaction with UC_2 is observed, the use of CrO_2Cl_2 was judged not to be feasible.

Ferric Chloride:

Two grams of $FeCl_3$, as vapor, had no effect on three grams of Type I fuel in two tests at 900°C. $FeCl_3$ falls into the same category as CrO_2Cl_2, and is likewise not feasible for employment as a chemical destruct reagent.

Carbon Tetrachloride:

Type I fuel specimens weighing 4 grams were subjected to 1-4 grams of CCl_4 vapor in the range 1000-2000°C. Some leaching of activity was observed but specimen integrity was unaffected and very little weight was lost. Therefore, the use of CCl_4 as a chemical destruct reagent is precluded.

Uranium Hexafluoride:

Since UF_6 vapor had been observed at LASL to destroy specimens completely at room temperature, tests were performed in the apparatus shown in Figure 1 in order to acquire quantitative data on the value of UF_6 as a chemical destruct agent. To three gram specimens of unlined, Type II fuel in vacuo were introduced approximately 1.0 gram

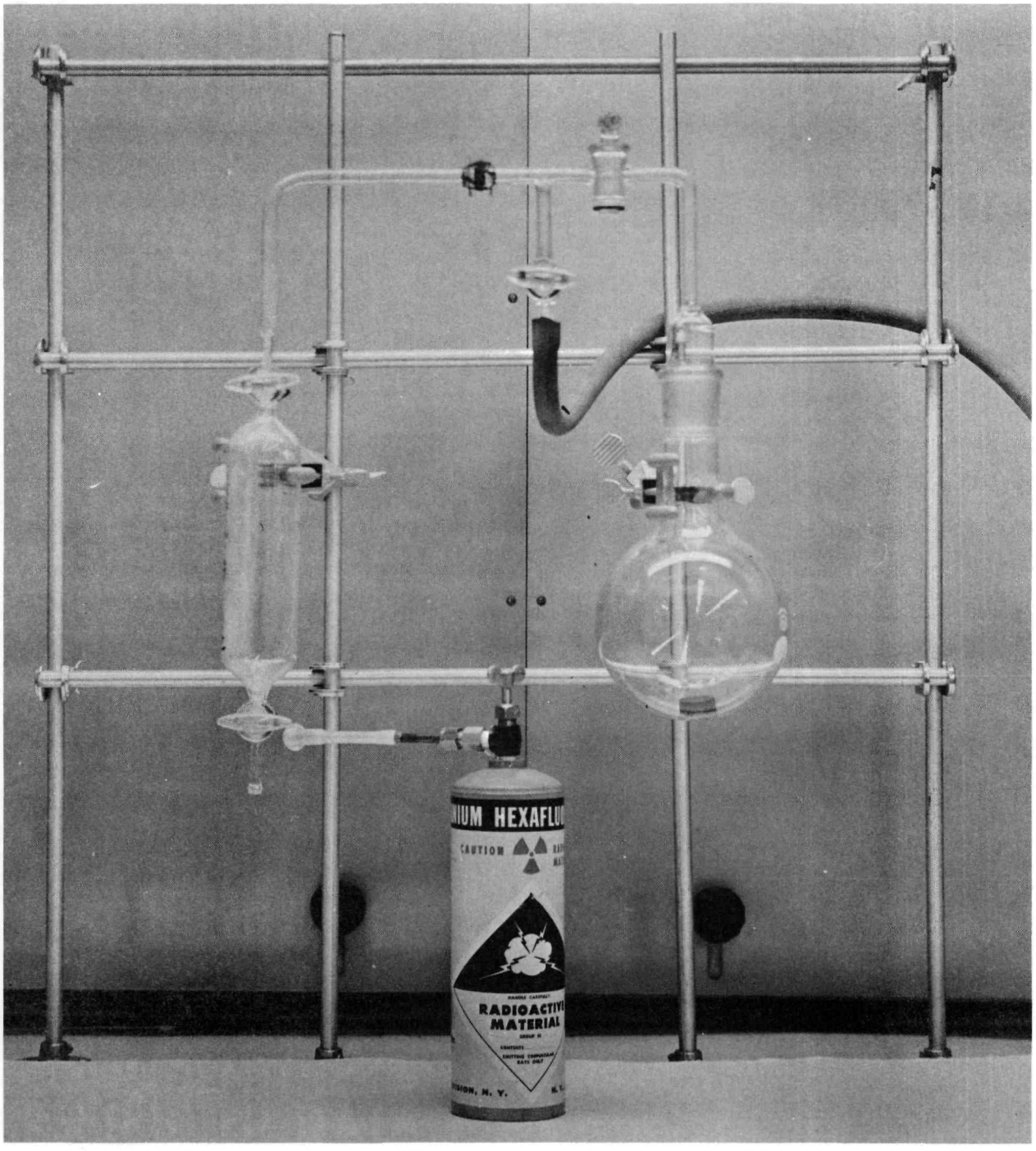

FIGURE 1 – APPARATUS FOR UF_6 TESTS

of UF_6 in tests at 25° and 300°C. In both cases, the UF_6 attacked the available surface of the specimen to form a compound of approximate composition $C_8(UF_6)$, which falls away from the solid core. These results imply that about 9000 pounds of UF_6 would be required for complete degradation of the core in this temperature range. In neither test had the intact portion absorbed a significant amount of UF_6, and the physical strength of this intact portion was comparable to that of unreacted material. It must also be recognized that the reaction between carbon and UF_6 does not take place above 450°C.

Potassium:

Potassium vapor had no affect on a three gram specimen of Type II fuel at 1500°C. This is consistent with the reported instability of potassium-graphite interstitial compounds above 350°C (Reference 4). Below 350°C, 1 gram of liquid potassium removed 1 gram of material from the specimen. Extrapolation of this result predicts that 2700 pounds of potassium would be required in a full scale system. Efficient utilization of potassium to form only C_8K in a vapor system might reduce this figure to 1000 pounds, although laboratory results indicate that long times would be required.

Fluorine:

The special apparatus shown in Figure 2 was designed and assembled especially for quantitative tests with fluorine in the range of 25-900°C. The specimen, a cross section of a Type II fuel element either 1/4 or 1/2 inch in thickness (weighing 3 or 6 grams) was placed inside a nickel ring in the center of the reaction tube so that fluorine was forced to flow through only the coolant channels in the specimen. A total of over twenty tests have been performed using fluorine and certain general conclusions may be drawn.

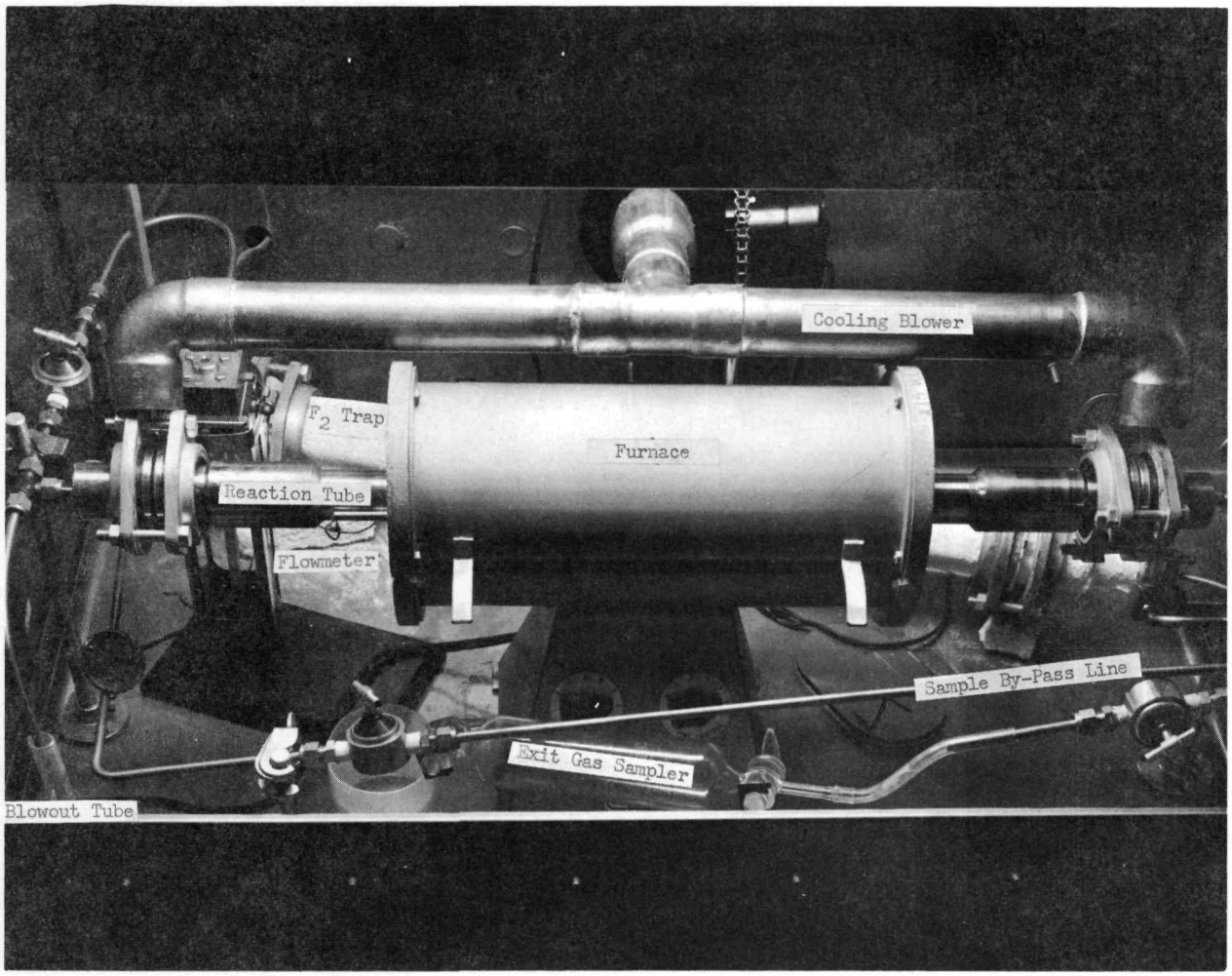

FIGURE 2

APPARATUS FOR FLUORINE TESTS IN
THE RANGE 25 - 900°C

1. At room temperature, the fuel is unaffected by fluorine except for a weight gain of a few milligrams on a 3 gram specimen from one gram of fluorine delivered over a period of five minutes.
2. In the range 250-400°C, fluorine absorption is rather more pronounced and subsequent heating to 700°C causes absorbed fluorine to form CF_4, a gas which tends to disrupt the structure. However, when the amount of fluorine flowed past the sample was held to 20-30% of the sample weight, only surface powdering was exhibited, leaving over 90% of the sample as a hard core.
3. Between 700 and 900°C, the sample burns in fluorine with complete consumption of the fluorine to form carbon fluorides and uranium fluorides. The behavior of the sample is independent of delivery rate between 0.1 and 1.0 grams of fluorine per minute and independent of HF contamination between 0 and 2% HF in fluorine. Extrapolation of these data indicates that the amount of fluorine required to completely consume the core in this temperature range would be approximately 6000 pounds. Experimental difficulties have limited testing to 1100°C. At this temperature the behavior of the fuel was identical to that at 800°C.
4. In addition, at least in the range 700-900°C, and probably over a wider range, niobium carbide presents no barrier to fluorine attack.

Interhalogens:

On the basis of encouraging qualitative tests, controlled amounts of BrF_3, BrF_5, IF_5, and ClF_3 were employed at temperatures up to 712°C with 2-5 gram specimens in a vacuum flow system. In these tests, which employed weights of reagent ranging from 5 to 100% of the specimen weight, the most promising exhibited complete powdering at 240°C of a 2.6 gram specimen of Type I fuel by 0.6 gram of ClF_3 delivered over a period of 60 minutes. A subsequent test employing a Type II fuel specimen under the same conditions resulted in less than ten percent weight loss from the specimen with no significant change in specimen strength. Reaction at high temperatures seems to depend on dissociation of the interhalogens followed by burning in the fluorine which is formed.

Nevertheless, if suitable pre-conditioning of the core could be accomplished, as little as 600 pounds of ClF_3 might be sufficient to degrade the entire core. Consequently, four larger scale tests were performed on nine inch long specimens of fuel weighing about 100 grams, which had been heat treated to degrade the pyrocarbon coatings on the UC_2 spheres.

In these tests, 40 grams of ClF_3 were flowed past the specimens over a period of one hour while the specimen temperature was maintained as close as possible to 240°C in vacuum. The system consisted of a pyrex tube in which the specimen was held and a thirty gallon ballast tank to maintain vacuum conditions. The entire system was evacuated to a few hundred microns pressure and sealed, whereupon ClF_3 was introduced at a rate of 175-200 cc per minute. The effluent of reaction products from the specimen flowed into the ballast tank. During the entire course of each test the pressure increased to less

than four inches of mercury, thus simulating space environment conditions more closely than in any previous test. The results of these tests are given in Table 1.

TABLE 1

RESULTS OF LARGE SCALE ClF_3 TESTS

Test No.	Specimen Pre-Treatment	Test Temperature	% Weight Loss
1	2400°C for 1 hour	200-280	24
2	2800°C for 2-1/2 hrs.	198-240	0
3	2800°C for 2-1/2 hrs.	227-242	15
4	2400°C for 1 hour	230-247	10

It is seen from the data in Table 1 that the favorable results of the test with a 2.6 gram specimen could not be duplicated. It was evident from the appearance of the nine inch specimens that channel clogging had occurred at an early stage in each test, forcing the ClF_3 to flow around the outside of the specimens. The fourth test was designed with a nickel ring filling in the annular space between the specimen and the glass wall in order to force ClF_3 to flow through the channels. The channels became blocked as before and ClF_3 broke through the specimen walls in this instance in escaping to the ballast tank. In all tests, then, channel blockage was followed by wasteful diversion of the ClF_3 stream.

In a full scale system, it maybe possible to avoid this phenomenon by introduction of ClF_3 at a higher pressure and speed, provided these changes do not bring about lowered efficiency due to shorter reagent residence time in the core.

Delivery System Concepts:

Additional work remains to be done to show whether the optimum estimated reagent weights of 600 pounds of ClF_3 and 1000 pounds of potassium are indeed achievable. Nevertheless, consideration has been given to both these reagents with regard to their availability and handling characteristics in a full scale destruct system.

Delivery Concept for Chlorine Trifluoride:

Chlorine trifluoride is available from General Chemical Division of Allied Chemical in ton quantities. At 25°C it is stored as a liquid under its own vapor pressure of 25 psia. Its density (113 lb/ft^3) allows a total storage capacity of only 6 cubic feet to suffice for the amount of reagent under consideration. Delivery of the reagent could be accomplished in a space environment by opening a valve and allowing the reagent to escape to the core under its own vapor pressure, which ranges from 1 psia at -40°C to 80 psia at 60°C. If rapid delivery is desired, a nickel clad electrical resistance heater should suffice, since the temperature of the liquid need be raised to only 100°C to elevate its vapor pressure to over 400 psia.

Acceptable materials of construction include copper, brass, and steel, although monel and nickel are preferred, the latter being suitable at higher temperatures. Valves in 1/2 inch and larger sizes, suitable for ClF_3 service, are available as shelf items.

Delivery Concept for Potassium:

Potassium is available in high purity and in large quantities. Unlike chlorine trifluoride, it is non-reactive with most metals and can be safely handled in steel. Storage of 1000 pounds of potassium would require a volume of about 20 cubic feet, still a small container by comparison to the overall system.

The principal engineering requirement of the system would be that of a heater to melt the potassium, raise its temperature to 300°C, and vaporize it. For 1000 pounds of potassium, a heat input of about 500,000 BTU would be required.

Hazards of Potassium and Chlorine Trifluoride:

Since these reagents are extremely reactive, the consequences of their accidental exposure to air, water, or liquid hydrogen must be considered. Such exposure may result in energy release and release of toxic products.

The following is a list of possible reactions which could occur[5] and the energy release from each of these[6], [7].

TABLE 2

Potassium and Chlorine Trifluoride
Possible Chemical Destruct Reactions Arising from Malfunctions

1. $K + O_2 \longrightarrow KO_2 + 67\ K\ cal/mole$
2. $K + H_2O \longrightarrow KOH + 1/2\ H_2 \xrightarrow{O_2} H_2O + 81\ K\ cal/mole$
3. $ClF_3 + 2\ H_2O \longrightarrow 3\ HF + 1/2\ O_2 + HOCl + 86\ K\ cal/mole$
4. $ClF_3 + 2H_2 \longrightarrow 3\ HF + HCl + 172\ K\ cal/mole$

Potassium will not react with liquid hydrogen and chlorine trifluoride will not react with air (except insofar as it reacts with water vapor in the air). Thus, the four reactions listed on the preceding page are the only reactions considered for the purpose of hazards estimation. Laboratory experiments indicate that destruct systems employing 2700 pounds of potassium or 600 pounds of chlorine trifluoride may merit consideration. These weights of reagents are assumed to react completely according to the four reactions listed above. The products of reactions are tabulated below.

TABLE 3

Potassium and Chlorine Trifluoride
Products of Reaction from Malfunction of Chemical Destruct Systems

Reaction	Energy Production	Toxic Material Produced
Potassium fire	8.2×10^6 BTU	4800 lb. of Potassium Superoxide Airborne
Potassium in water and H_2 fire	10^7 BTU	3850 lb. of Caustic Potash in sea
ClF_3 in water	1.0×10^6 BTU	400 lb. of Hydrogen Fluoride in sea
ClF_3 - Hydrogen fire	2.0×10^6 BTU	240 lb. of Hydrogen Chloride airborne plus 400 lb. of Hydrogen Fluoride Airborne

Conclusions & Recommendations:

Table 4 gives estimated minimum reagent weights in full scale chemical destruct systems based on extrapolation of the test results obtained with gram quantities of core

material. Further testing must be done before these figures can be quoted with confidence. Table 5 includes engineering considerations applicable to a number of concepts. The use of Type II fuel has negated preferential reaction with UC_2 unless the core is pre-conditioned to destroy the protective pyrocarbon coatings. As a result, reagents introduced into a core of Type II fuel would be forced to degrade the core by reacting completely with more than a ton of graphite. This is largely responsible for the substantial weight requirements shown in Table II. In summary, no reagent tested thus far indicates promise for employment in a post operational chemical destruct system of relatively light weight which is independent of temperature and compatible with Type II fuel. However, laboratory results indicate that with pyrocarbon coating destruction followed by core cooling to the vicinity of 240°C, as little as 600 pounds of chlorine trifluoride could produce complete core degradation. Potassium may accomplish this result with about 1000 pounds of material. The salient points with respect to these systems are enumerated below.

1. The degradation products of the core would be particles of essentially zero velocity vector and uniformly small size. In laboratory tests, the maximum particle dimension was less than one millimeter.
2. The engineering difficulty of effecting thermal pre-treatment to degrade the pyrocarbon coatings and/or NbC linings, a cooling cycle to reduce the core temperature to about 240°C, and the efficient introduction of the reagents must be evaluated in comparison to that of other proposed destruct systems.

TABLE 4

CHEMICAL DESTRUCT LABORATORY TEST EXTRAPOLATIONS
25-2000°C

List of Reagents with Estimated Minimum Reagent Weight in Full Scale System

Non-Halides	Halides
O_2 - 6000 lb	HF - Prohibitive*
H_2O - Prohibitive*	HCl - Prohibitive*
H_2O_2 - Prohibitive*	Cl_2 - Prohibitive*
HNO_3 - Prohibitive*	BCl_3 - Prohibitive*
N_2 - Prohibitive*	CrO_2Cl_2 - Prohibitive*
K -1000-2700 lb< 350°C	$FeCl_3$ - Prohibitive*
	BBr_3 - 4000 lbs. at 1000°C only
	Br_2 - 6000 lbs. at 2000°C only

Freons

CF_4 - Prohibitive*

CCl_3F - Prohibitive*

CCl_2F_2 - Prohibitive*

*Weight of reagent equal to that of sample left>90% of sample intact.

Fluorine and Fluorides

	High Temp. > 400°C (1200°R)	Low Temp. <400°C (1200°R)
F_2	6,000 lb.	Prohibitive without subsequent nuclear transient
BrF_3	14,000 lb.	Prohibitive
BrF_5	10,000 lb.	2000 lb.
ClF_3	8,000 lb.	650 lb.
IF_5	14,000 lb.	4000 lb.
UF_6	Prohibitive*	9000 lb.

TABLE 5

SUMMARY OF CHEM. DESTRUCT CONCEPTS

Reagent	Estimated Weight Required	Preconditioned or Operational Limit.	Hazards
Oxygen	6,000 lb.	Preheat $>$ 3,000°R	Potential Expl. Mixture non-toxic products
Oxygen	12,000 lb.	1,950° - 3,000°R	
Fluorine	6,000 lb.	None	Potential Expl. Toxic products + Materials
Bromine	6,000 lb.	Remove pyrocoat	Toxic potential expl.
Boron Tribromide	4,000 lb.	Remove pyrocoat T $<$ 2,200°R Matl. Availability	Toxic
UF_6	9,000 lb.	T $<$ 1,250°R	Toxic
Chlorine Trifluoride	600 lb.	Remove pyrocoat T $<$ 900°R	Toxic Potentially Explosive
Potassium	1,000 to 2,700 lb.	Heat reagent T $<$ 1000°R	Toxic Expl. in Contact with water

3. Afterheat will be available to raise the core temperature and excess propellant can be made available for subsequent core cooling.

4. As for handling of chlorine trifluoride and potassium, these compounds have in recent years emerged from the category of laboratory curiosity and are now readily available in ton quantities and amenable to relatively simple handling procedures even at elevated temperatures.

5. The potential ground hazard of a chlorine trifluoride or potassium system must be considered, but should be evaluated in comparison to potential hazards from other destruct systems under consideration. The employment of fluorine in propulsion systems is under serious study and such a system would involve potential hazards at least as great as those of the systems described here.

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